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The accomplished research has involved (1) the construction of new instrumentation for the investigation of transient high energy materials; (2) the exploration of how the chemistry of transient high energy materials is modified by adsorption on the surfaces at interfaces; and (3) the exploration of how the chemistry and dynamics of high energy density materials respond to systematic variations in structure, and experimental variables such as pressure, magnetic fields and temperature. Particular emphasis has been given to reactions in microheterogeneous environments and interfaces provided by micelles, polymers and porous solids. Since the initiation of this grant, a time resolved electron spin resonance spectrometer and a time resolved NMR spectrometer capable of measuring CIDNP spectra on a routine basis have been constructed.

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DYNAMICS AND STABILIZATION OF MATERIALS POSSESSING HIGH ENERGY CONTENT

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Columbia University

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DYNAMICS AND STABILIZATION OF MATERIALS POSSESSING HIGH ENERGY CONTENT

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FINAL REPORT

Dynamics and Stabilization of Materials Possessing High Energy Content

SUMMARY: The accomplished research has involved (1) the construction of new instrumentation for the investigation of transient high energy materials ; (2) the exploration of how the chemistry of transient high energy materials is modified by adsorption on the surfaces at interfaces; and (3) the exploration of how the chemistry and dynamics of high energy density materials respond to systematic variations in structure, and experimental variables such as pressure, magnetic fields and temperature. Particular emphasis has been given to reactions in microheterogeneous environments and interfaces provided by micelles, polymers and porous solids. Since the initiation of this grant, a time resolved resonance Raman spectrometer, a time resolved electron spin resonance spectrometer and a time resolved NMR spectrometer capable of measuring CIDNP (Chemically Induced Dynamic Nuclear Polarization) spectra on a routine basis have been constructed.

High Energy Materials Adsorbed on Porous Solids

The photochemistry of ketones adsorbed on the internal surface of porous solids, such as silica and zeolites, was found to vary dramatically from that observed in homogeneous solution. The basis for the differing behavior has been traced to the control of the diffusional and rotational properties of the intermediate radicals produced by photolysis of the ketones. For example, it was shown that photochemical reactions of ketones adsorbed on zeolite molecular sieves can be controlled dramatically by the number density, charge and size of exchangeable cations associated with the zeolite framework (427, 435, 440, 443). The dramatic influence of site, geometry and size on the diffusion of radicals on zeolite surfaces was demonstrated for the important family of ZSM-5 zeolites (421).

The products could be varied systematically by varying the silicon to aluminum content and the amount of water adsorbed by the zeolite. The role of surfaces in controlling the reactions of high energy species was strikingly demonstrated by the observation that photochlorination of straight chain hydrocarbons adsorbed on ZSM-5 zeolites occurs selectively at the terminal position, whereas photochlorination of same materials in solution results in completely non-selective chlorination at all positions (424). The quenching of triplet state benzophenone adsorbed on porous silica by oxygen has been investigated by time resolved diffuse reflectance laser spectroscopy. Diffusion within the restricted pore geometry of a series of silica was modeled as a target annihilation reaction in three dimensions (425, 426), and a general scaling behavior was found that related the rate of the annihilation to the characteristic mean pore size of the silica. The scaling behavior was found to be that predicted by a simple random walk of the oxygen molecules diffusing within the pore space. The direct observation of benzyl radicals produced by photolysis of dibenzyl ketone adsorbed on porous silica by electron spin resonance was achieved (419). The size of the silica pores and the presence and absence of water were found to influence the observed spectra in a manner consistent with the occurrence of two bound forms of the radicals, on a freely diffusing surface species and the other a more tighly bound surface species. Excited state resonance Raman spectroscopy has been shown to be a sensitive technique to characterize the hemicelles which are formed when surfactants are adsorbed from aqueous solvents onto porous solids (432). Ru(II) complexes were employed as photoluminescence probes which were shown to be sensitive to the solid liquid interface produced by formation of the hemimicelles. Research on photoluminescent metals was extended to ruthenium complexes (437). Dramatic magnetic isotope and magnetic field effects on the product distribution of photolysis of dibenzyl ketone adsorbed on zeolites were discovered (442). An extension of the research on photochemistry of molecules adsorbed on porous solids was made to solid complexes of ketones and aqueous solutions of stilbene and cyclodextrins (444, 446)

Structure and Dynamics of High Energy Reactive Intermediates

A time resolved laser spectroscopic investigation of the interaction of triplet enones with ethylenes has provided kinetic evidence for the mechanism of this important class of photoreactions (431). The pressure dependence of the mechanism of the cycloaddition of ethylene to ketones was investigated (429). The first example of hyperconjugation in directing the selectivity of photoreactions was discovered (430). An investigation of the photochemistry of benzocyclobutene was shown to yield isomeric products that result from a rearrangement of a photochemically produced high energy benzene isomer to a carbene (423). These results provide insight into the role of energy surfaces in interconverting species of enormous energy content. The influence of molecular geometry on the spectroscopic and photochemical properties of a series of benzophenone cyclophanes was investigated (441). A novel method for the investigation of electron spin transfer through spin polarization transfer to a stable nitroxide was invented (447). The first investigation of the pressure induced variation in the diastereoselectivity in photoinduced Diels-Alder reactions was reported (448).

Radicals and Biradicals

Nanosecond transient absorption studies of the lifetimes of several substituted biradicals elucidated the mechanisms which determine the lifetime of these reactive intermediates (422, 436, 438, 439). It was established that spin-orbit coupling provides the major mechanism for intersystem crossing when the biradical possesses an acyl radical center and that nuclear-electron hyperfine coupling provide the mechanism for intersystem crossing when a hydrocarbon biradical is generated. The lifetime of a hydrocarbon biradical was found to depend on the presence of lanthanide (III) ions. No net reaction occurred. It was proposed that an electron spin exchange between the biradicals is responsible for the quenching of the biradical. These results demonstrate the ability to manipulate

the lifetimes of high energy species by inert quenchers whose structures and efficiencies of quenching can be varied. The importance of the size of the hyperfine constant in determining CIDNP effects was determined (445).

Polymers

A review of the use of photoluminescence and spin methods as probes of polymer interfaces and structures was published (417). Examples from AFOSR supported research on the binding, conformation and association of water soluble polymers were emphasized.

II. Coupling Activities

In July 1989 Dr. Don Ball visited our laboratories and was involved in detailed discussions of our current research activities. At the V International Symposium on Inclusion Phenomena and Molecular Recognition in September 1988 in Orange Beach, Alabama, the principal investigator and Dr. Larry Burggraf were involved in several extended discussions concerning the use of photochemical methods to attack problems in interface science. The possible use of Dr. Burggraf's novel method of using specifically shaped holes to control photochemical processes was explored.

The Principal Investigator was presented with a major award during 1988: The James Flack Norris Award in Physical Organic Chemistry of the Northeastern Section of the American Chemical Society. He was the "Frontiers in Chemical Research Lecturer" at Texas A&M University (May 1988) and presented a series of lectures at the Royal Institute of Technology in Stockholm (May 1988) and presented a lecture at a workshop on Photochemistry of Polymers sponsored by the European Polymer Federation in Stockholm. He also presented lectures at Caltech, UCLA, Berkeley, University of California at Fullerton, New York University, University of

Washington, University of Victoria (Canada) and University of British Columbia (Canada), Rohm and Haas, Ciba-Geigy and E. I. DuPont. He presented papers at the Gordon Research Conference on Physical-Organic Chemistry, the Gordon Research Conference on Organic Photochemistry, the Inter-American Photochemical Society, the American Chemical Society in Miami Beach (Polymer Division and Physical Chemistry Division)

The Principal Investigator is the co-Chairman of the National Academy of Sciences Board on Chemical Sciences and Technology, and he serves on an Advisory Committee to the Chemistry Division of the Office of Naval Research and on the Science Advisory Committee of the Council for Chemical Research. He also serves on the Advisory Boards of the **Journal of the Americal Chemical Society, the Journal of Photochemistry, the Journal of Reactive Intermediates, Langmuir, and the Encyclopedia of Physical Science and Technology.**

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Nicholas J. Turro November 6, 1989

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